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The Review of the Doctoral Thesis entitled **“Synthesis, spectroscopic analysis, and exploration of applications for heterocyclic molecular systems exhibiting photo and chemiluminescence phenomena”**, written by **MSc. Vladyslav Ievtukhov** under the scientific supervision of **Dr. Sc. Karol Krzyński, Prof. UG**, and **Dr. Sc. Illia E. Serdiuk, Prof. UG**.

1. Formal grounds for the review

The formal and legal grounds for reviewing the doctoral dissertation of **MSc. Vladyslav Ievtukhov** is receiving a letter (**L.dz.T000-ISZ/WCh-1203/25**) from **Prof. DSc. Zbigniew Kaczyński**, the Chairman of the **Scientific Council of Chemical Sciences at Gdańsk University**, with a request to evaluate the above-mentioned doctoral dissertation (based on the Act of 20 July 2018 – The Law on Higher Education and Science).

2. Basic information about the thesis and its structure.

The doctoral thesis was completed in the **Faculty of Chemistry and the Faculty of Mathematics, Physics, and Informatics of Gdańsk University** under the joint supervision of **Dr. Sc. Karol Krzyński, Prof. UG**, and **Dr. Sc. Illia E. Serdiuk, Prof. UG** – the auxiliary supervisor. The entire PhD thesis has a multidisciplinary character, encompassing areas of research such as chemistry, physics, materials science, and materials engineering.

It takes the form of a topically coherent collection of scientific papers, comprising three research articles from the ISI Master Journal List and Ministerial List of Journals. In my opinion, a selected form of the PhD thesis is justified, especially because all three papers comprehensively describe a full set of research, spanning from synthesis to potential applications, with a strong modeling component providing the understanding of physical and chemical backgrounds of the investigated types of materials and their luminescence.

The dissertation begins with acknowledgments and a list of abbreviations, followed by a list of publications comprising the doctoral thesis, a list of other notable achievements, a second set of acknowledgments (in this case, referring to co-founders), and abstracts in both Polish and English. Next, in the Introduction section, the Reader is introduced to the topic of luminescence and nitrogen-containing heterocyclic molecules, where the Author also justifies the undertaken research. Then, the two research areas explored in the thesis are introduced and explained, along with details regarding the significance of the conducted studies. The first one refers to the chemiluminescence of acridinium-based molecules, and the second one is devoted to the explanation of the TADF effect in the TMCz-BO compound. Both sections describe the state-of-the-art of research undertaken within the thesis. Next, the Reader is





familiarized with the hypotheses and work objectives, and then can find a detailed description of the performed experiments, the obtained results, and the conclusions drawn during the dissertation's realization. All of these details are described in two sections, "Part I Acridinium salts as indicators in luminescence studies" and "Part II Spectroscopic and computational studies of the TADF mechanism of the TMCz-BO compound as a promising deep-blue emitter for OLED technology", which refer to the previously described research topics, where the state of the art of research is introduced. The entire PhD thesis is finished with conclusions, literature, and the three scientific articles mentioned earlier.

The entire doctoral dissertation structure lacks a classical approach, where the introduction, state of the art, significance, methodology, and results are described in their own separate sections. Here, most of the mentioned details seem to be grouped into two topics, each described separately. Such an approach can be seen as quite unusual (even in the case of a coherent collection of papers); however, in my opinion, it does not hinder the Reader from obtaining the most important information from the text and understanding the research's importance.

To summarize this part, the doctoral thesis is written in good English and is easy to understand; moreover, the research carried out and described within is of high importance (see next report sections). However, it is struggling with some formatting issues that could be easily fixed by allocating a minimal amount of time to address them.

- For example, citations: [1,2,3,4,5,6,7] can be replaced by [1-7], and figure references are present in both forms: "Fig." and "Figure". I also found a reference to the incorrect or non-existent figure (Fig. 6, which should possibly be Fig. 7) on page 31.
- I also think it would be more informative if the reaction presented in Fig. 7 had been referring directly to the molecule described in the text. In text, we have 4NO₂-ATE; in Fig. 7, we deal with H-ATE.
- In abstracts, both in Polish and English, Part Ia and Part Ib should have been permuted, as in the thesis body, their content is reversed. Possibly, the entire thesis was designed to have the reversed order of the [P1] and [P2] papers; however, they were somehow incorrectly attached.
- Renaming of the one section from *Acknowledgements*, for example, to *Acknowledgements to cofounders* could allow avoiding having two identical names for different sections.
- Formatting inconsistencies are also present; for example, not the whole text is justified. This is evident on page 16, and pages 17 to 18 have a "to the left" formatting.
- Finally, the structures of the particular sections are also inconsistent. For example, in "thematic area I", we have a subsection titled "Topicality of 1st problem," and then in the second part, we have just "topicality." Finally, the "topicality" subsection is not present in "thematic area II."
- Another issue that needs to be pointed out here refers to the Research Hypotheses section: Most of the "hypotheses" listed there can actually be classified as objectives or aims. In general, in my opinion, the list of objectives and aims is rather too long. Additionally, different aims are distributed across various sections and subsections (for example, on page 17, the primary





objective of research becomes a task in the *Work Objectives* section), causing confusion regarding which aim is more important and what the hierarchy between them is.

- *At the end of this part of the report, I would like to ask MSc. Vladyslav Ievtukhov to formulate one or two main theses of this dissertation.*

3. Scope and the significance of the scientific problems described in the dissertation.

The scope of the PhD thesis revolves around the synthesis and utilization of nitrogen-containing heterocyclic molecules that exhibit efficient chemiluminescence and TADF effects.

The topic of chemiluminescence is addressed in two papers [P1] and [P2], where the first describes the synthesis of aromatic acridinium thioesters and their potential application in detecting biologically significant antioxidants. The research is enriched by the proposition of reaction schemes leading to chemiluminescence of the studied compounds. The second one is devoted to the potential utilization of 9-CMA acridinium salt in the detection of sulfur-containing nucleophiles. Similar to the previous case, the reaction schemes explaining the chemiluminescence mechanism are also proposed – in both cases, they are based on DFT calculations. Finally, LOD and QOD parameters, essential for sensing capabilities, were determined, demonstrating the potential applicability of the studied and synthesized compounds described in [P1] and [P2].

The last paper [P3], which is topically separate from the previously described one, is related to the TADF behavior of the TMCz-BO compound. The topic of TADF molecules is particularly important in OLED technology, especially in the context of developing deep blue emitters. The TMCz-BO compound exhibits blue and highly efficient emission, making it a suitable candidate for OLED technologies. Importantly, the examined TMCz-BO compound exhibits a complex photophysical dependence on environmental conditions, including viscosity and polarity, which is explained in terms of dynamic and static excited-state mixing models.

To summarize this part, it is essential to note that each of the mentioned research activities was conducted comprehensively, and the investigated molecules were not only characterized in terms of their optical properties, but their potential applications were also identified or tested, and finally, the mechanisms explaining the physical and chemical background of luminescence were also proposed.

4. Methodology

The full information about the methodology is not available in the descriptive part of the thesis. The Reader is then referred to specific sections and articles that compose the whole dissertation. In general, the methodology used in the research is, in my opinion, sufficient for the scientific research carried out within the PhD thesis, for the assumed aims, and to draw the proper conclusions. It can be divided into:

- (i) **Synthesis:** 6 acridinium thioesters and 9-CMA⁺ were synthesized as entirely new compounds; TMCz-BO was synthesized according to a previously described procedure available from the literature.





Purification was carried out using column chromatography and TLC. Mass, ^1H NMR, ^{13}C NMR, and IR spectroscopic studies were used to identify the structures of the synthesized compounds.

The synthetic methods and techniques used for structure confirmation are typical for organic chemistry and are sufficient.

- (ii) **Spectroscopy:** This part of the methodology combined the classical UV-Vis spectroscopy with advanced spectroscopic techniques involving emission measurements as a function of temperature, including cryogenic temperatures. PL lifetime measurements were performed using a custom system comprising a pulse laser and a streak camera. Chemiluminescence was measured using a specialized luminometer for chemiluminescence measurements. Emission QYs were assessed with the aid of the integrating spheres.

The methodological background of spectroscopy is at a very high level and is entirely sufficient for the aims of the research carried out within the dissertation.

- (iii) **Sensing:** For sensing purposes regarding articles [P1] and [P2], a spectroscopic approach utilizing luminometers for chemiluminescence measurements was used. In the case of biologically important antioxidants, two thioesters were tested: 4NO₂-ATE and 2MeO-ATE. The presence of antioxidants and the quenching of chemiluminescence were analyzed, enabling their detection. Regarding the [P2] article, the 9-CMA⁺ chemiluminescent molecule was tested against biologically important nucleophiles containing a sulfur atom, such as NAC, DPA, GSH, and ATC. In this case, the presence of nucleophiles resulted in an increase in chemiluminescence intensity. The results were compared to Lucigenine, indicating the superiority of 9-CMA⁺ over the mentioned reference compound.

In my opinion, the methodology described here is sufficient for the first screening of materials for potential sensing applications. However, since, in the case of [P1], the sensing is based on the quenching of chemiluminescence intensity, I believe that more detailed studies regarding the specificity of this process are needed in the future. Regarding the [P2] article, I also have some concerns about the specificity of the method used here, as the presence of nucleophiles supports an oxidation process leading to 9-CMA⁺ chemiluminescence. Thus, I have two remarks here:

- Quenching of emission is not a specific phenomenon. It can be caused by the reabsorption of various chemical compounds present in the analyzed sample, especially those of biological origin. Please specify the types of tests currently used in biochemical laboratories





for which your idea is suitable, or at least indicate how this problem could be solved. A similar remark can be formulated for the influence of nucleophiles on 9-CMA⁺ chemiluminescence.

- *It would be very informative for the Reader to specify what concentrations of biologically important antioxidants and sulfur-containing nucleophiles are expected in potential tests, particularly in the environments in which the detection will be carried out. In other words, I would like to ask if the obtained detection ranges are practical for monitoring some biologically important processes, or if they require some adjustment.*

- (iv) **Quantum-chemical calculations:** performed in collaboration with Dr. Beata Zadykowicz, are based on well-known and frequently utilized DFT and TD-DFT methods. It was used to identify proper reaction mechanisms leading to chemiluminescence for compounds described in [P1] and [P2]. It is important to underline that MSc. Vladyslav Ievtukhov wasn't directly involved in the quantum-chemical calculations; however, in my opinion, this does not in any way diminish his contribution to the development of models explaining chemiluminescence.

I think the methods utilized here are also sufficient to get insight into the physical and chemical background of chemiluminescence and the TADF effect.

- *However, I am unable to find the information about who was responsible for the quantum-chemical calculations related to the [P3] article. It should be clarified.*

5. Main achievements:

- **Synthesis** of 6 new acridinium thioesters with potential sensing capability of biologically important antioxidants and conformation of their chemical structures.
- **Development** of reaction pathways influencing thioesters chemiluminescence in the presence of the antioxidants.
- **Synthesis** of acridinium salt for the potential sensing capability of biologically important nucleophiles containing sulfur with increased chemiluminescence intensity vs Lucigenin.
- **Development** of reaction pathways influencing acridinium salt chemiluminescence in the presence of the antioxidants.
- **Investigation** of the TMCz-BO's complex photophysical behavior leading to its complete understanding.
- **Development** of a dynamic and static excited-states mixing model explaining the nature of remarkable triplet harvesting in TMCz-BO-based systems.





6. Strengths and weaknesses of the doctoral thesis, and questions and remarks on particular papers

Strengths:

- Easy to read and understand.
- Well-described state of the art and importance of the research, the Reader is nicely introduced into the topic of heterocyclic molecules used for various types of luminescence.
- Very good scientific soundness.
- Very good methodological background.
- Addressing an important, but not frequently studied, topic of chemiluminescence.
- Potential importance of research regarding biosensing and applications in OLEDs and lightning technologies.
- Material characterization supported with significant insight into photophysical and chemical background.

Weaknesses:

- Formatting issues, lack of uniform structure of particular sections, etc.
- Lack of strictly formulated hypotheses.
- Too many aims, distributed within different thesis sections without an easily recognizable hierarchy.

7. Other questions and remarks

[P1] and [P2]:

- *Can you provide chemiluminescence spectra for compounds studied regarding [P1] and [P2]? Can they differ for a single compound if a different antioxidant/nucleophile is present?*

[P3]:

- *Can you provide CIE1937 coordinates and diagrams for TMCz-BO? It exhibits a considerable solvatochromic effect; therefore, obtaining a deep blue emission might require the use of an optimal host. Please comment on that, referring to the definition of deep-blue emission by the European Broadcasting Union and/or the National Television System Committee.*
- *Do you observe the TICT effect for the TMCz-BO molecule? It seems that molecular design suggests that this effect is possible. What about the emission from crystalline or powdered samples? Do you observe any Aggregation-Induced Emission Enhancement effect for this molecule?*





8. Conclusions and summary

To conclude, despite some formatting issues, the dissertation demonstrates a good level of scientific soundness; the results presented in the thesis are recent and of high significance to the scientific and technical community. Especially, I would like to emphasize that the topic of chemiluminescence is not frequently addressed by the scientific community, which typically focuses its attention on photoluminescence and electroluminescence. The development of new and more efficient chemiluminescent materials with biosensing potential is, therefore, a huge achievement. The same could be stated regarding the development of dynamical excited-state mixing and static excited-state mixing models to explain the complex TADF behavior of the TMCz-BO compound in various environments. The problems described in the doctoral thesis are, undoubtedly, original and have been published in three high-level scientific journals from the Ministerial List of Journals and the ISI Master Journal List. The Author can also boast of authorship of an article published in a very prestigious *Chemical Sciences* journal, as well as being the owner of one Polish patent application.

To summarize, MSc. Vladyslav levtukhov, up to now (according to the Research Gate website - 01.10.2025), has published seven regular articles in highly valued journals, including *Chemical Sciences*, *Journal of Materials Chemistry C*, etc., and three conference papers, which were cited 45 times. His H-index is equal to 3, and he is the owner of one patent application. Moreover, MSc. Vladyslav levtukhov has attended multiple domestic and international conferences, actively contributing to the Polish and Worldwide scientific community. Therefore, based on the evaluation of Mr. Vladyslav levtukhov's doctoral thesis and his scientific achievements, I am convinced that he has acquired all the knowledge and qualifications necessary for independent scientific work within the field of **Chemical Sciences**.

The doctoral thesis submitted for evaluation meets all formal requirements for candidates for doctoral degrees specified in the Act of 20 July 2018 —The Law on Higher Education and Science. Therefore, I request that the thesis be admitted to the defense and that the author be allowed to proceed to the further stages of the doctoral procedure.

Finally, referring to the attached Regulations for Doctoral theses distinction in Chemical Sciences, I find the scientific achievements of MSc. Vladyslav levtukhov is sufficient to fulfill the requirements of the distinguished theses. The PhD candidate has presented three scientific papers, which comprise the PhD thesis, representing the Q1 and Q2 quartiles in the chemical sciences. Moreover, the PhD candidate presented an approach to science typical for a mature scientist searching for a deep understanding of the phenomena that they are working on. His additional scientific portfolio, not strictly related to the PhD thesis, also demonstrates a much wider range of scientific interests and the necessity to seek other scientific inspirations to shape his own career. Thus, I find MSc. Vladyslav levtukhov is a promising young scientist with extreme development potential to reach the top league of worldwide researchers.

Hence, I recommend the Doctoral Thesis of MSc. Vladyslav levtukhov, entitled "Synthesis, spectroscopic analysis, and exploration of applications for heterocyclic molecular systems exhibiting photo and chemiluminescence phenomena", written





9. Wnioski końcowe i podsumowanie

Pomimo pewnych niedociągnięć edytorskich pracy, rozprawa doktorska wykazuje bardzo wysoki poziom rzetelności naukowej. Przedstawione w niej wyniki są aktualne i mają duże znaczenie dla społeczności zainteresowanej wokół badań naukowych i prac technologicznych. W szczególności chciałbym podkreślić, że temat chemiluminescencji nie jest często poruszany przez środowisko naukowe, które zazwyczaj koncentruje się na takich zjawiskach jak fotoluminescencja i elektroluminescencja. Opracowanie nowych i bardziej efektywnych materiałów chemiluminescencyjnych mogących znaleźć zastosowanie w konstrukcji bio-czujników stanowi znaczące osiągnięcie naukowe. Podobnie należy ocenić rozwój modeli dynamicznego i statycznego mieszania stanów wzbudzonych, mających na celu wyjaśnienie złożonego zachowania TADF związku TMCz-BO w różnych środowiskach, zarówno ciekłych jak i stałych. Problemy opisane w rozprawie doktorskiej są bez wątpienia oryginalne i zostały opublikowane w trzech wysoko cenionych czasopismach naukowych z Ministerialnej Listy Czasopism Punktowanych oraz z ISI Master Journal List. Autor może również pochwalić się publikacją w bardzo prestiżowym czasopiśmie *Chemical Sciences*, a także krajowym zgłoszeniem patentowym.

Podsumowując, mgr Vladyslav levtukhov, według danych z portalu Research Gate (stan na 01.10.2025), opublikował dotychczas siedem artykułów naukowych w renomowanych czasopismach, takich jak *Chemical Sciences*, czy *Journal of Materials Chemistry C*, oraz trzy publikacje konferencyjne. Artykuły były do tej pory cytowane aż 45 razy, a indeks H Pana mgr. Vladyslava levtukhova wynosi 3. Na uwagę zasługuje również fakt złożenia jednego zgłoszenia patentowego. Ponadto mgr Vladyslav levtukhov uczestniczył w wielu konferencjach o zasięgu krajowym i międzynarodowym, aktywnie przyczyniając się do rozwoju polskiej i światowej społeczności naukowej. Dlatego też, na podstawie oceny rozprawy doktorskiej Pana Vladyslava levtukhova oraz jego osiągnięć naukowych, jestem przekonany, że zdobył on wystarczającą wiedzę i kwalifikacje niezbędne do samodzielnej pracy naukowej w dziedzinie nauk chemicznych.

Złożona do oceny rozprawa doktorska spełnia wszystkie formalne wymagania, określone w ustawie z dnia 20 lipca 2018 r. „Prawo o szkolnictwie wyższym i nauce” odnośnie możliwości uzyskania stopnia naukowego doktora. W związku z tym wnoszę o dopuszczenie rozprawy doktorskiej do obrony oraz umożliwienie Panu Vladyslavowi levtukhovi uczestnictwa w kolejnych etapach przewodu doktorskiego.

Na zakończenie, odnosząc się do wymagań w załączonym, Regulaminie wyróżniania rozpraw doktorskich w dziedzinie nauk chemicznych (Uchwała nr 164/RD/23 z dnia 08.11.2023r.), uważam, że osiągnięcia naukowe Pana mgr Vladyslava levtukhova są wystarczające, aby je spełnić. Kandydat przedstawił trzy publikacje naukowe, które składają się na rozprawę doktorską i reprezentują czasopisma skasyfikowane w kwartylach Q1 i Q2, w dziedzinie nauk chemicznych, według klasyfikacji Scopus. Ponadto kandydat zaprezentował podejście do nauki typowe dla dojrzałego badacza, poszukującego głębokiego zrozumienia zjawisk, nad którymi pracuje. Dodatkowo, jego bogate naukowe portfolio, niezwiązane bezpośrednio z rozprawą doktorską, świadczy o znacznie szerszym zakresie zainteresowań badawczych oraz potrzebie poszukiwania innych inspiracji naukowych w celu kształtowania własnej ścieżki kariery akademickiej. Dlatego też uważam, że mgr Vladyslav levtukhov jest





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obiecującym młodym badaczem o ogromnym potencjale pozwalającym na dołączenie do grona najlepszych naukowców w kraju i za granicą.

W związku z powyższym rekomenduję **wyróżnienie rozprawy doktorskiej** mgr Vladyslava levtukhova pt. „Synteza, analiza spektroskopowa i eksploracja zastosowań heterocyklicznych układów molekularnych wykazujących zjawiska foto i chemiluminescencji”, napisanej pod opieką naukową dr hab. Karola Krzymińskiego, prof. UG, oraz dr hab. Illii E. Serdiuka, prof. UG.

02.10.2025 Wrocław

Dr. Sc. Eng. Lech Sznitko

